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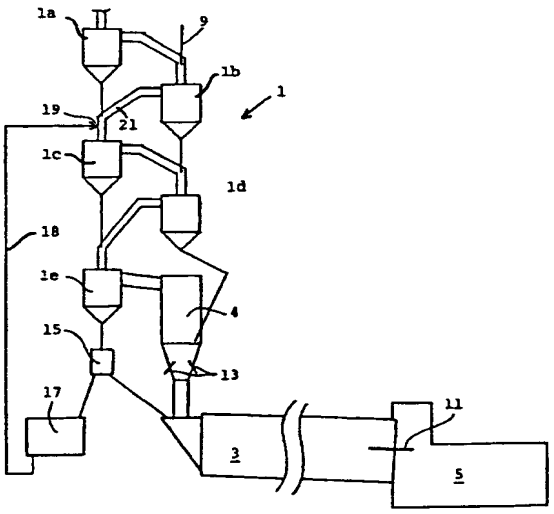
(54) Title: METHOD AND APPARATUS FOR DESULPHURISATION OF EXHAUST GASES



(57) Abstract: Described is a method and apparatus for desulphurisation of exhaust gases from a cement making plant by bonding gaseous sulphur dioxide to calcium-containing cement raw meal which is extracted from the calcination stage (4) of the plant and subsequently brought into contact with the exhaust gases as a sulphur-absorbing reactant. The specific method slaking and grinding the extracted raw meal prior to it being brought into contact with the exhaust gases. By this method and apparatus an improvement of the thermal economy, is obtained by reducing the quantity of raw meal required for the desulphurisation process. This is ascribable to the fact that by subjecting the raw meal to slaking and grinding, the fineness of the raw meal will be improved, thereby enhancing the efficiency of the desulphurisation process.

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METHOD AND APPARATUS FOR DESULPHURISATION OF EXHAUST GASES

The present invention relates to a method and apparatus for desulphurisation of exhaust gases from a cement making plant by bonding gaseous sulphur dioxide to calcium-containing cement raw meal which is extracted from the calcination stage of the plant and subsequently brought into contact with the exhaust gases as a sulphur-absorbing reactant.

A method of this kind is known from US–A-4,634,583. The disadvantage of this known method is its low rate of efficiency. This is due to the fact that the particle size of the calcined raw meal which is introduce into the exhaust gases is relatively large, causing its surface area to be reduced correspondingly. Therefore, this known method requires much more raw meal than is theoretically required, leading to an unnecessary waste of heat since the extracted raw meal is cooled from a temperature range between 850 and 950° to a temperature range of 220 - 250°C.

It is the object of the present invention to provide a method and apparatus by means of which the mentioned disadvantage is reduced.

According to the invention this object is achieved by a method of the kind mentioned in the introduction and being characterized in that the extracted raw meal is slaked and ground prior to being brought into contact with the exhaust gases.

An improvement of the thermal economy is thereby obtained by reducing the quantity of raw meal required for the desulphurisation process. This is ascribable to the fact that by subjecting the raw meal to slaking and grinding, the fineness of the raw meal will be improved, thereby enhancing the efficiency of the desulphurisation process. Tests conducted have indicated that a reduction of the particle size of the reactant will enhance the rate of efficiency of the desulphurisation process.

It is preferred that a substantial amount of the calcium oxide (CaO) contained in the extracted raw meal is converted into calcium hydroxide ($Ca(OH)_2$), due to the greater capability of the latter to bond sulphur dioxide (SO_2). According to the invention it is therefore preferred that the extracted, calcined raw meal is subjected to minimum 80 per cent slaking, and preferably full-scale slaking. The percentage of slaking is determined to be equal to (1 - free CaO after slaking/free CaO before slaking) x 100, where free CaO is reported on an ignition-loss free basis as is conventional.

Since a reduction in the particle size of the reactant will raise the efficiency of the desulphurisation process, it is further preferred that the extracted, calcined raw meal is ground to an average particle size of less than 5 µm, preferably of less than 3 µm.

The invention also includes apparatus for desulphurisation of exhaust gases from a cement making plant, having means for slaking and for grinding the extracted raw meal prior to bringing it into contact with the exhaust gases.

It is particularly in cases where sulphides, such as pyrite (FeS_2), are incorporated in the raw materials that the exhaust gases from the cement making plant contains SO_2. SO_2 is formed by partial oxidation for example of FeS_2, at around 550°C. Furthermore, the highest efficiency of desulphurisation when using extracted raw meal is achieved at high temperatures. It is therefore preferred that the extracted, calcined raw meal is introduced into the exhaust gas stream at a location immediately after, viewed in the direction of flow of the exhaust gases, SO_2 has been formed by partial combustion of the sulphide constituents in the raw materials. In a traditional cement making plant comprising a preheater with five cyclone stages, the formation of SO_2 from sulphide-containing raw materials will typically take place in the inlet duct for the third cyclone stage and in that cyclone stage itself. In such a plant it is preferred that the extracted raw meal is introduced into the exhaust gases in the exhaust gas discharge duct from the third cyclone stage or at a subsequent location. In actual practice, SO_2 measuring equipment will be used to establish exactly where SO_2 is formed, with the decision concerning the location of the point of introduction being made accordingly.

It is preferred that the extracted, calcined raw meal in a flash pipe is introduced into a stream of mixed air and water causing it to be slaked, that the slaked raw meal is separated in a separating mechanism, and is subsequently conveyed to and ground in a mill.

It is further preferred that the airstream from the flash pipe is used to convey the slaked and ground, calcined raw meal from the mill to the point of introduction.

The overriding objective of the present invention is to remove the SO_2 originating from the raw materials because the SO_2 formed from the fuels in the hotter parts of the kiln system is effectively bonded to CaO and converted into $CaSO_4$ which is a solid which will be a constituent component of the finished clinker.

In the following the invention will be explained in further detail with reference to the accompanying diagrammatical drawings, in which:-

Figure1 shows a traditional cement making plant where the method according to the invention is used; and

Figure. 2 shows an especially preferred embodiment of the invention.

In Figure 1 is seen a cement making plant which comprises a cyclone preheater 1 with five cyclones 1a to 1e, a calciner 4, a rotary kiln 3 and a clinker cooler 5. The

plant is run in accordance with traditional operating principles which involves raw material being introduced at an inlet 9 in the inlet duct to the first cyclone stage 1a of the cyclone preheater and heated, calcined and burned into clinker by first being directed through the preheater 1, the calciner 4 and subsequently through the kiln 3 in counterflow with hot exhaust gases which are formed at, respectively, a burner 11 in the rotary kiln 3 and burners 13 in the calciner 4. The burned clinker is subsequently cooled in the clinker cooler 5.

In accordance with the method of the invention, some of the hot, calcined raw meal is extracted from the fifth stage separating cyclone 1e of the preheater 1 by means of a dosing mechanism 15 which is designed for extracting a controlled stream of material. The stream of material thus extracted is directed to a slaking and grinding apparatus 17 of any suitable kind. For example, this could be a ball mill, a vertical mill, a ring roller mill or a roller press to which water (H_2O) is added, possibly in vaporized form. In an especially preferred embodiment of the invention the apparatus 17, as shown in Fig. 2, comprises a riser pipe or flash pipe 17a with a subsequent separating cyclone 17b and a mill 17c. In this embodiment the extracted, calcined raw meal is introduced into an ascending stream of mixed air and water, thereby causing the raw meal to be slaked. The air is supplied by means of a fan 16 and the water is supplied via an opening 20. The slaked, but still substantially dry, calcined raw meal is subsequently separated in the separating cyclone 17b from where it is conveyed, if convenient via an intermediate bin (not shown) to the mill 17c wherein it is ground to the desired particle size.

From the apparatus 17 the now slaked and ground, calcined raw meal is conveyed, possibly via a scoop device, to an entrance opening 19 which is provided in the outlet duct 21 of the third cyclone stage 1c. In the embodiment shown in Fig. 2, the raw meal is conveyed pneumatically via a duct 18 by means of the airstream from the flash pipe.

After being introduced into the exhaust gases, calcium oxide (CaO) and calcium hydroxide ($Ca(OH)_2$) will react with the SO_2 present in the exhaust gases and will be converted into calcium sulphite $CaSO_3$ and/or calcium sulphate $CaSO_4$. These solids may be a constituent part of the clinker in similarity with other constituent components of the raw materials.

The slaked and ground, calcined raw meal may either be conveyed direct to the entrance opening 19 or it may be conveyed to an intermediate bin, not shown, wherefrom it may subsequently be led by means of a dosing means to the entrance opening. The actual introduction of the material may take place using a special lance

which is capable of dispersing the slaked and ground, calcined raw meal across the entire cross-sectional area of the duct 21 in order to optimize the efficiency of the desulphurisation process.

CLAIMS

1. A method for desulphurisation of exhaust gases from a cement making plant by bonding gaseous sulphur dioxide to calcium-containing cement raw meal which is extracted from the calcination stage (4) of the plant and subsequently brought into contact with the exhaust gases as a sulphur-absorbing reactant, **characterized in** that the extracted raw meal is slaked and ground (17) prior to being brought into contact with the exhaust gases.

2. A method according to claim 1, **characterized in** that the extracted, calcined raw meal is subjected to a minimum of 80 per cent slaking.

3. A method according to claim 1 or claim 2, **characterized in** that the extracted, calcined raw meal is subjected to full-scale slaking.

4. A method according to any of claims 1 to 3, **characterized in** that the extracted, calcined raw meal is ground to an average particle size of less than 5 µm.

5. A method according to claim 4, **characterized in** that the extracted, calcined raw meal is ground to an average particle size of less than 3 µm.

6. A method according to any of claims 1 to 5, **characterized in** that the extracted, calcined raw meal is introduced into the exhaust gas stream at a location (19), viewed in the direction of flow of the exhaust gases, immediately after SO_2 has been formed by partial combustion of the sulphide constituents in the raw materials.

7. A method according to any of claims 1 to 6, **characterized in** that the extracted, calcined raw meal is introduced into a stream of mixed air and water in a flash pipe (17a), causing it to be slaked, that the slaked raw meal is separated in a separating mechanism (17b), and is subsequently conveyed to and ground in a mill (17c).

8. A method according to claim 7, **characterized in** that the airstream from the flash pipe (17a) is used to convey the slaked and ground, calcined raw meal from the mill (17c) to the point of introduction (19) into the exhaust gases.

9. An apparatus for desulphurisation of exhaust gases from a cement making plant by a method of bonding gaseous sulphur dioxide to calcium-containing cement raw meal which is extracted from the calcination stage (4) of the plant and subsequently brought into contact with the exhaust gases as a sulphur-absorbing reactant, **characterized by** means (17) for slaking and for grinding the extracted raw meal prior to bringing it into contact with the exhaust gases.

10. Apparatus according to claim 9, **characterized by** means (18) for introducing the extracted, calcined raw meal into the exhaust gas stream at a location (19), viewed in the direction of flow of the exhaust gases, immediately after SO_2 has been formed by partial combustion of the sulphide constituents in the raw materials.

11. Apparatus according to claim 9 or claim 10, **characterized in that** the means for slaking the extracted, calcined raw meal includes a flash pipe (17a).

12. Apparatus according to claim 11, **characterized in that** the means for slaking the extracted, calcined raw meal includes a separating mechanism (17b).

13. Apparatus according to claim 11 or claim 12, **characterized in that** the means for grinding the extracted, calcined raw meal includes a grinding mill (17c).

14. Apparatus according to claim 13, **characterized in that** a duct (18) is used to provide an airstream from the flash pipe (17a) to convey the slaked and ground, calcined raw meal from the mill (17c) to the point of introduction (19) into the exhaust gases.

15. A cement making plant having apparatus according to any of claims 9 to 14.

16. A cement making plant according to claim 15, including a five-stage preheater, **characterized in that** the slaked and ground raw meal is introduced into the exhaust gases immediately prior to the third stage (1c) of the preheater (1).

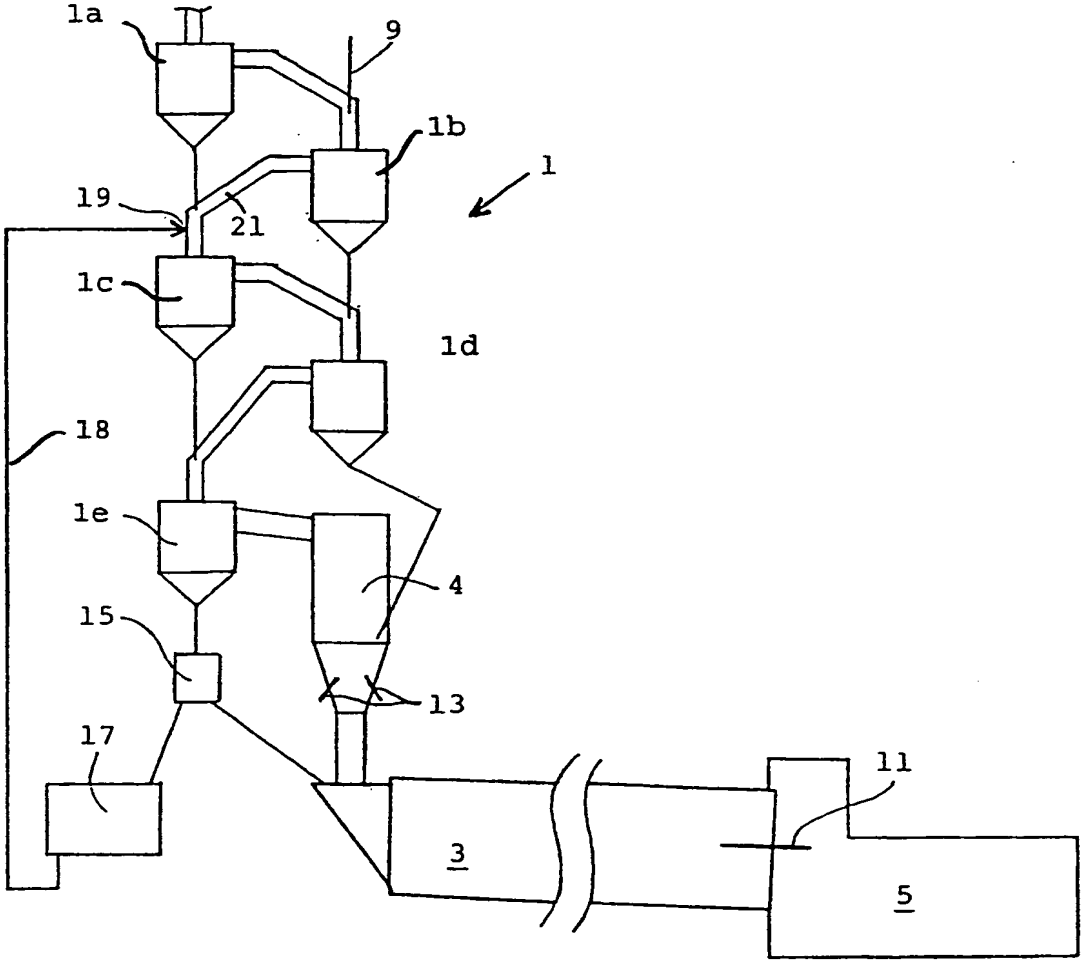
1a
9
1b
1
19
21
1c
1d
18
1e
4
15
13
17
11
3
5

Fig. 1.

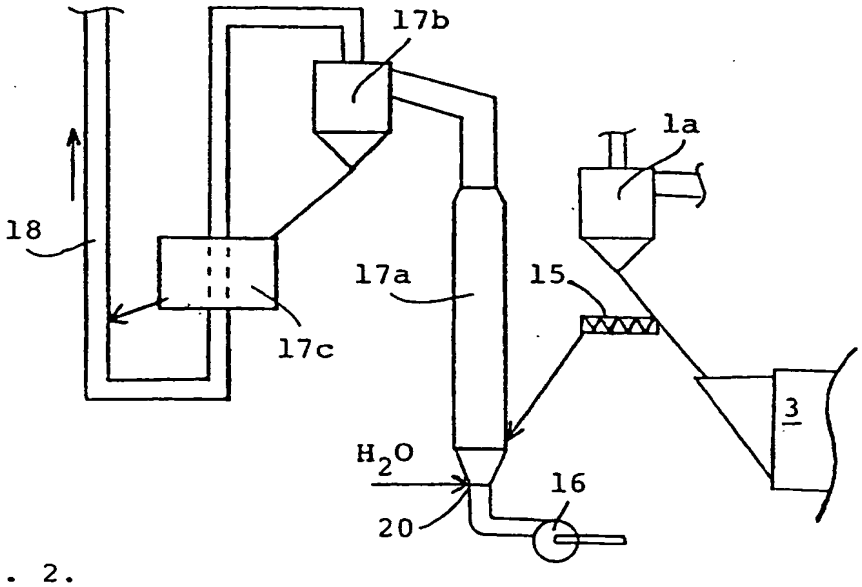
17b
1a
18
17a
15
17c
3
H_2O
16
20

Fig. 2.

INTERNATIONAL SEARCH REPORT

Int tional Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D53/50 B01D53/83

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	DE 36 43 143 A (KRUPP POLYSIUS AG) 11 May 1988 (1988-05-11) claim 1	1,9,12, 13,15 2,3,10
X A	US 4 634 583 A (WOLTER ALBRECHT ET AL) 6 January 1987 (1987-01-06) cited in the application column 2, line 52 - line 61; claims 1,4,6	1,9,12, 13,15 6,10
X	EP 0 845 443 A (SCHWENK BAUSTOFFWERKE KG E) 3 June 1998 (1998-06-03) claims 1,6	1
A	WO 93 10884 A (SMIDTH & CO AS F L) 10 June 1993 (1993-06-10) abstract	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
3 October 2000	10/10/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Faria, C

INTERNATIONAL SEARCH REPORT

Int: ional Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 228 111 A (METALLGESELLSCHAFT AG) 8 July 1987 (1987-07-08) column 2, line 48 - line 55	1

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte ional Application No
PCT/EP 00/05880

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

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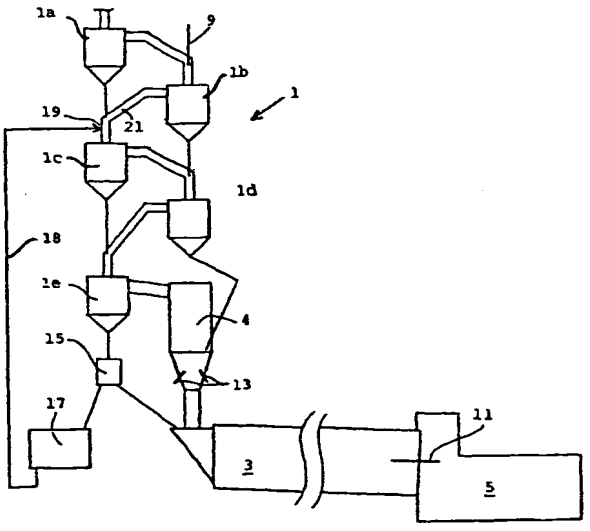
[Continued on next page]

(54) Title: METHOD AND APPARATUS FOR DESULPHURISATION OF EXHAUST GASES



(57) Abstract: Described is a method and apparatus for desulphurisation of exhaust gases from a cement making plant by bonding gaseous sulphur dioxide to calcium-containing cement raw meal which is extracted from the calcination stage (4) of the plant and subsequently brought into contact with the exhaust gases as a sulphur-absorbing reactant. The specific method slaking and grinding the extracted raw meal prior to it being brought into contact with the exhaust gases. By this method and apparatus an improvement of the thermal economy, is obtained by reducing the quantity of raw meal required for the desulphurisation process. This is ascribable to the fact that by subjecting the raw meal to slaking and grinding, the fineness of the raw meal will be improved, thereby enhancing the efficiency of the desulphurisation process.

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AMENDED CLAIMS

[received by the International Bureau on 7 December 2000 (07.12.00);
original claim 9 amended; remaining claims unchanged (2 pages)]

1. A method for desulphurisation of exhaust gases from a cement making plant by bonding gaseous sulphur dioxide to calcium-containing cement raw meal which is extracted from the calcination stage (4) of the plant, slaked and subsequently brought into contact with the exhaust gases as a sulphur-absorbing reactant, **characterized in** that the extracted raw meal is ground (17) prior to being brought into contact with the exhaust gases.

2. A method according to claim 1, **characterized in** that the extracted, calcined raw meal is subjected to a minimum of 80 per cent slaking.

3. A method according to claim 1 or claim 2, **characterized in** that the extracted, calcined raw meal is subjected to full-scale slaking.

4. A method according to any of claims 1 to 3, **characterized in** that the extracted, calcined raw meal is ground to an average particle size of less than 5 µm.

5. A method according to claim 4, **characterized in** that the extracted, calcined raw meal is ground to an average particle size of less than 3 µm.

6. A method according to any of claims 1 to 5, **characterized in** that the extracted, calcined raw meal is introduced into the exhaust gas stream at a location (19), viewed in the direction of flow of the exhaust gases, immediately after SO_2 has been formed by partial combustion of the sulphide constituents in the raw materials.

7. A method according to any of claims 1 to 6, **characterized in** that the extracted, calcined raw meal is introduced into a stream of mixed air and water in a flash pipe (17a), causing it to be slaked, that the slaked raw meal is separated in a separating mechanism (17b), and is subsequently conveyed to and ground in a mill (17c).

8. A method according to claim 7, **characterized in** that the airstream from the flash pipe (17a) is used to convey the slaked and ground, calcined raw meal from the mill (17c) to the point of introduction (19) into the exhaust gases.

9. An apparatus for desulphurisation of exhaust gases from a cement making plant by a method of bonding gaseous sulphur dioxide to calcium-containing cement raw meal, the apparatus including means for slaking the extracted raw meal prior to bringing it into contact with the exhaust gases, whereby the cement raw meal is extracted from the calcination stage (4) of the plant, slaked, and subsequently brought into contact with the exhaust gases as a sulphur absorbing reactant, **characterized by** means for grinding the extracted raw meal prior to bringing it into contact with the exhaust gases.

10. Apparatus according to claim 9, **characterized by** means (18) for introducing the extracted, calcined raw meal into the exhaust gas stream at a location (19), viewed in the direction of flow of the exhaust gases, immediately after SO_2 has been formed by partial combustion of the sulphide constituents in the raw materials.

11. Apparatus according to claim 9 or claim 10, **characterized in that** the means for slaking the extracted, calcined raw meal includes a flash pipe (17a).

12. Apparatus according to claim 11, **characterized in that** the means for slaking the extracted, calcined raw meal includes a separating mechanism (17b).

13. Apparatus according to claim 11 or claim 12, **characterized in that** the means for grinding the extracted, calcined raw meal includes a grinding mill (17c).

14. Apparatus according to claim 13, **characterized in that** a duct (18) is used to provide an airstream from the flash pipe (17a) to convey the slaked and ground, calcined raw meal from the mill (17c) to the point of introduction (19) into the exhaust gases.

15. A cement making plant having apparatus according to any of claims 9 to 14.

16. A cement making plant according to claim 15, including a five-stage preheater, **characterized in that** the slaked and ground raw meal is introduced into the exhaust gases immediately prior to the third stage (1c) of the preheater (1).